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UPGRADING OF PYROLYSIS OIL INTO DIESEL-LIKE FUEL OIL: COMPARISON BETWEEN IN-SITU AND EX-SITU TEST RIG

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Abstract. Upgrading of pyrolysis oil to petrochemical products is favorable as these products are more easily accepted in the existing energy infrastructure. Pyrolysis oil derived from pyrolyzing examination rubber gloves was catalytically upgraded over zeolite using two different rigs namely *in situ* test rig and *ex situ* test rig. In the *in situ* test rig, chemical composition of the upgraded oil was similar to the black thermal pyrolysis oil. This is due to the presence of moisture in the primary pyrolysis gas, as well as due to the macromolecular structure of the ester compounds that prohibit entrance into the cation site of the zeolite. Meanwhile, upgrading of pyrolysis oil in the *ex situ* test rig produced yellow colour oil. Polyaromatic hydrocarbon compounds of 3-ring and 4-ring benzene compounds were absent in this upgraded oil. It was observed that the pyrolysis oil was de-oxygenated by the action of the zeolites resulting in straight chain hydrocarbons that emulate diesel fuel. The main composition of the upgraded oil remained to be 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester. Although the black pyrolysis oil can be upgraded, but the yield of diesel-like fuel oil reduced considerably.

Keywords: Pyrolysis; upgrading; fuel-oil; diesel; zeolite

Abstrak. Minyak yang terhasil dari proses pirolisis ditingkatkan kepada produk menyerupai petroleum memandangkan produk sebegini lebih mudah diterima dalam struktur tenaga sedia ada. Dalam kajian ini, proses peningkatan minyak pirolisis yang terhasil daripada pirolisis sarung tangan getah telah dijalankan menggunakan dua unit pelantar pengujian yang dikenali sebagai pelantar pengujian *in situ* dan *ex situ*. Proses peningkatan ini menggunakan katalis zeolit. Kajian menggunakan pelantar pengujian *in situ* mendapati bahawa komposisi kimia minyak adalah tidak berubah daripada minyak pirolisis asal. Ini adalah disebabkan kandungan kelembapan dan juga saiz makro molekul yang besar yang menghalang capaian ke kation di dalam zeolit. Sebaliknya, lebih banyak akuas yang terhasil yang terdiri daripada fenol dan asid karbosilik. Kajian peningkatan minyak menggunakan pelantar pengujian *ex situ* menghasilkan minyak berwarna kuning. Ini menunjukkan minyak asal telah dinyahoksida melalui tindakan zeolit lalu menghasilkan sebatian hidrokarbon lurus yang bersamaan dengan kandungan minyak diesel.

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Sebatian utama masih tetap 1, asid 2-Benzenedicarboxylic, bis(2-ethylhexyl) ester. Walaupun minyak pirolisis boleh dipertingkatkan menjadi diesel, tetapi penghasilan secara keseluruhannya adalah rendah.

Kata kunci:: Pirolisis; peningkatan; bahan api; diesel; zeolite

1.0 INTRODUCTION

Pyrolysis seems to be a simple and efficient method to produce gasoline and diesel-like fuels [1]. The pyrolysis of natural rubber (cis-1,4-polyisoprene) or the pure elastomer has been carried out previously by many researchers [2,3,4]. The major products in the oil were the monomer, isoprene, and the dimmer, dipentene, with other oligomers up to hexamer in significant concentration. Attractively, some of the derived products could be valuable [5]. It is desirable that the oil derived from pyrolysis could be upgraded to a product that look more like petroleum hydrocarbons so that the end use device would require little or no modification. Experience on pyrolysis oil derived from biomass, known as bio-oil, shows that bio-oil requires upgrading due to its viscosity, thermal instability, corrosiveness and chemical complexity [6]. The upgrading techniques that can be employed include catalytic hydrodeoxygenation, emulsification, steam reforming and catalytic esterification.

Previously, pyrolysis of examination rubber gloves was studied by Hall *et. al* [7] and Zakaria *et. al* [8] as pyrolysis is deemed as a suitable alternative treatment process for medical waste [9]. Pyrolysis of rubber gloves conducted in the Integral Pyrolysis Test Plant developed in the Malaysian Nuclear Agency produced black oil, water, char, gas and tar [8]. The properties of the black pyrolysis oil are as in Table 1. The oil was found to be acidic with substantial amount of sulphur of that 20wt%. The oil also contained some water at 4% vol/vol. Interestingly, the oil derived from pyrolysis of rubber gloves has a high energy value of 42 MJ/kg with very low ash content of 0.028wt %.

Judging from these characteristics, clearly the quality of the pyrolysis oil derived from the pyrolysis of rubber gloves is way off from the commercial fuel specifications thus, the quality of the pyro-oil need to be further improved in order to suit as a potential candidate for an alternative liquid fuel. Generally, the presence of catalyst in the pyrolysis process resulted in higher proportions of light hydrocarbons compounds and subsequent reduction in the oil fraction [10]. For this purpose, different types of catalysts acidic, like silica-alumina or zeolite (HY, HZSM-5, mordenite) as well as alkaline compounds such as ZnO, CaO, K_2O have been used [12]. Presence of Y zeolite in the pyrolysis process has been found to increase the aromatic content of the derived fuel [13,14] whereas HZSM Zeolites was found effective to deoxygenate bio-oil [15]. The temperature factor has no significant effect on the pyrolyzates when catalytic pyrolysis is concerned. Bagri and William pyrolysed polyethylene over a zeolite HZSM5 and HY catalysts and found that the use of zeolites increased the aromatic content of the derived fuel [13]. Seo et. al. stated that zeolites enhanced the formation of aromatics and branched hydrocarbons while amorphous silica-alumina showed a great activity on cracking High Density Polyethylene (HDPE) to lighter olefins [14].

Table 1 Properties of pyrolysis oil from examination rubber gloves pyrolysis

Parameter	Properties
kinematic viscosity	11.22 cps
ash content	0.028 wt%
pH	3.13
sulfur content	19.87 wt%
chlorine content	1.32 wt%
water content	4 vol%
calorific value	42.4 MJ/kg

Catalytic pyrolysis process can be carried out either by *in situ* or *ex situ* configuration. In *ex situ* configuration the black pyrolysis oil was thermally cracked, i.e reheated, and the gases evolved were then passed through a catalyst bed. This practice has been exercised by Seng *et. al* (2006) in upgrading bio-oil derived from oil palm shell [16]. This configuration is different from *in situ* configuration whereby in the *in situ* process, the primary pyro-vapors passed through the catalyst bed prior to condensation. Lima *et. al* [15] suggested that pyrolysis oil derived from wood pyrolysis can catalytically be deoxygenated using different zeolites [15]. Thus, it is inferred that the pyro-oil derived from the rubber gloves can be upgraded over catalyst. Therefore it is to the interest of the study to evaluate the feasibility of upgrading pyro-oil derived form pyrolyzing rubber gloves over zeolite by *in situ* and *ex situ* configurations.

2.0 MATERIALS AND METHOD

2.1 Reactors

An *in situ* and *ex situ* catalyst rigs were developed in this study to suit the different nature of the starting material. The first one was a stainless steel reactor that was attached to the Integral Pyrolysis Test Plant and was being referred to as *in situ* test rig as shown in Figure 1. In this rig, one batch of 500 grams of un-shredded rubber gloves was used as the feed material. Rubber gloves were fed into the pyrolysis reactor via top loading once the reactor had reached the desired operating temperature. The second test rig was called as *ex situ* rig which was assembled using glassware. Figure 2 shows the schematic diagram for *ex-situ* test rig. In this rig, the black oil which was originally produced from thermal pyrolysis of rubber gloves of the Integral Pyrolysis Test Plant was dripped onto a sampling boat. The boat containing the black pyrolysis oil was then being inserted into the reactor before the temperature was ramped to reach the selected operating temperature. Due to the reactor size, the feed throughput was limited to 3 grams of oil. At least three runs were carried out for each temperature selected and the average yield was determined. The operating temperature selected for *in situ* rig was 400°C, while a temperature of 200°C, 250°C and 300°C was employed in the *ex situ* rig.

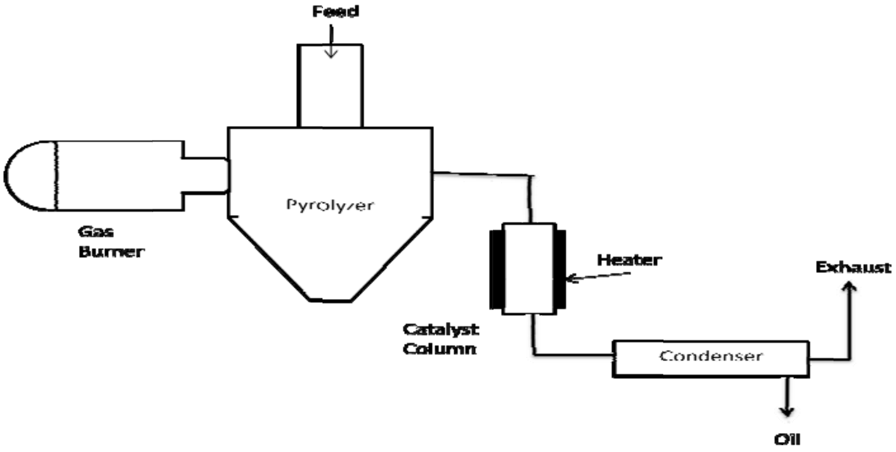

Figure 1 Schematic diagram of *in situ* test rig attached to the pyrolyzer of the integral pyrolysis test plant

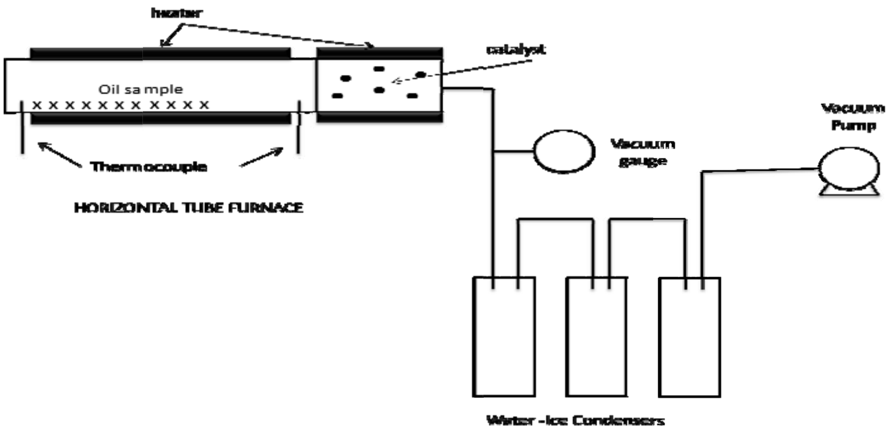

Figure 2 Schematic diagram of *ex situ* test rig

2.2 Catalyst

Each catalyst cage in the *in situ* and *ex situ* rig is loaded fully with extruded catalyst and conditioned at 400°C prior usage. The type of catalyst used was CBV 780 CY (1.6mm average diameter) Zeolite SDUSY Extrudate obtained from Zeolyst International. This catalyst appeared in the form of white rods, 1.6 mm diameter and odorless. The catalyst has the following characteristics:, SiO_2/Al_2O_3 ratio 80, 0.03 weight% Na_2O, 780 m^2/g surface area, and hydrogen as the nominal cation form.

2.3 Gas Chromatography Mass Spectrometer (GC-MS)

Gas Chromatography Mass Spectrometer (GC-MS) (model Shimadzu QP5050A) was used to speciate the pyrolitic oil. The column used was ZB-1 (30m × 0.25 mm). The identification of the compounds was made by comparing to the library of the GC-MS as well as from standard diesel mixture obtained from Supelco and a known standard containing 17 compounds of straight chain alkane hydrocarbon comprising of C_{12}, C_{14}, C_{16}, C_{17}, Pristane, $C_{18:1}$, C_{18}, Phytane, C_{20}, C_{21}, C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, C_{32} and C_{34}.The temperature program used was as follows: Starting temperature 45°C, hold for 3 minutes, then the temperature was ramped to 300°C, at 7.5°C/min. The final temperature (300°C) was hold for 5 minutes. An aliquot of the oil was injected into the GCMS using splitless mode. The oil was diluted using ethyl acetate solvent of HPLC grade.

2.4 Fourier Transform Infra-red Analysis (FTIR)

FTIR analysis of the pyrolysis oils was recorded on Perkin-Elmer P/N 10500 series spectrometer using Single Reflection Diamond ATR technique. Scanning was made from absorption wavelength of 4000 cm^{-1} to 600 cm^{-1}. The absorption band identification was based on 3 aspects, namely the intensity (weak, medium, or strong), shape (broad or sharp) and position (cm^{-1}) in the spectrum.

3.0 RESULTS AND DISCUSSIONS

3.1 Yield

Table 2 summarized the pyrolysis products obtained when rubber gloves were catalytically pyrolyzed in the Integral Test Plant employing *in situ* configuration. From naked eye observation, the color of the oil was similar to the color of the oil produced thermal, non-catalytic pyrolysis, i.e dark brown to black. Although there was no change in the color appearance, the profound difference between catalytic and non-catalytic pyrolysis of rubber gloves at the Integral Pyrolysis Test Plant is the amount of aqueous. More aqueous was formed during the catalytic pyrolysis as compared to the non-catalytic pyrolysis. The amount of aqueous and the oil were 46.8% and 36.8% respectively. Besides aqueous, another by-products that was formed during the catalytic pyrolysis in the Integral Test Plant was tar. In this study, tar was defined as the deposits on the catalysts and along the reactor wall while char was the carbon black in the sand of the reaction bed. The amount of tar and char was 1.54 wt% and 4.33 wt% respectively. The amount of uncondensable gas was calculated out to be 10.0 wt%.

Table 2 Yield of pyrolysate from rubber gloves pyrolysis at 400°C with *in situ* test rig installed

Pyrolysate Products	Composition (wt%)	
Solid Products	Tar	1.54
	Char	4.33
Liquid Products	Oil	36.80
	Aqueous	46.78
Gas (by difference)		10.55
Total		100.00

Meanwhile, when the black pyrolysis oil was upgraded in *ex situ* test rig, yellowish oil condensate was observed. In this configuration, the black oil was reheated and the gases evolved were passed through the catalyst bed, producing yellow color oil which was collected in the condenser, leaving thin layer of dry residue in the sampling boat. Deposit of tar was also observed in the catalyst bed. The overall mass balance for *ex situ* upgrading study was tabulated in Table 3. The results showed that at 300°C, 37.5% of the black oil was upgraded into yellowish oil, leaving 34.6% residue and 27.9% gas. There was an increase in the oil yield recorded as the temperature was raised from 200°C to 300°C. In *ex situ* configuration, upgrading of the oil is achieved in two step processes which are the thermal pyrolysis and the catalyst upgrading, whereas in *in situ* configuration, upgrading of the oil is achieved in a single step process as thermal pyrolysis and the catalyst upgrading takes place in the same system. The mass balance suggests that the yield of oil was further reduced when the oil was upgraded employing ex-situ configuration. The mass balance analysis indicated that the if the oil was to be upgraded using *ex situ* configuration, then from the raw material (in this case, rubber gloves) of 1000 grams, the amount of diesel-fuel like that is likely to be produced is 174 grams, giving an overall yield of 17.4%.

Table 3 Yield of upgraded oil, solid and gas in the *ex situ* test rig

Operating Temperature	**Upgraded Oil (wt%)**	**Tar and Solid Residue (wt %)**	**Gas * (wt%)**
200°C	29.8	50.8	19.4
250°C	35.4	42.5	22.1
300°C	37.5	34.6	27.9

Note: * calculated by difference to make up 100%.

3.2 Chemical Composition of the Catalytic Pyrolysis Oil

The compounds speciated in the catalytic pyrolysis oil produced in the in-situ test rig of the Integral Pyrolyis Test Plant are presented in Table 4. The main compounds in the oil was found to be 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester. As compared to the study conducted by Hall *et.al* [7], when y-zeolite catalyst was added to the reaction system, the composition of the pyrolysis oil changed considerably, with limonene being most eliminated and a large increase in the yield of single and multiple ring aromatics. However, the profile of the catalytic oil in this study was found to be similar to the oil derived during the thermal pyrolysis and no significance changes were observed between these two profiles. This could be due to the presence of moisture or water vapor presence in the pyro-gas prior condensation. Water vapor has known to have an influence on the adsorption of volatile compounds onto zeolite as the water molecules occupy the available sites of the zeolite [18]. Moisture also solvates the cation and localizes the cations on preferred sites on the lattice [19]. Thus, the presence of moisture makes the y-zeolite catalyst ineffective. Besides the presence of moisture, no catalytic conversion is expected over y-zeolites due to molecules like phtalic acid and esters which are larger than the catalyst pores. As such, these molecules cannot reach the cations in the inner surface of the catalyst pores [6]. These two factors; moisture and molecular size, has made the catalyst ineffective in the Integral Test Plant thus justify for the unchanged oil composition.

When analyzed using FTIR, the similarities between the oil obtained during thermal pyrolysis and the catalytic pyrolysis, both running in the Integral Test Plant, were further confirmed. Figure 3 shows the FTIR spectra of the catalytically upgraded oil in the in-situ test rig of the Integral Pyrolysis Test Plant. Presence of aromatic compounds was reflected by the absorption bands at 3700cm^{-1} and was further confirmed from the presence of absorption bands between 915cm^{-1} to 650cm^{-1}. Also, the sharp and strong band at 1517cm^{-1} can be associated to the aromatic nucleus. Thus, the FTIR analysis suggests that the addition of y-zeolite catalyst has promoted formation of aromatic compounds in this study considerably. The doublet at 2921cm^{-1} indicates the presence of CH_3 and CH_2 while the strong band at 1453cm^{-1} and 1375cm^{-1} can be associated to the methylene and methyl deformation respectively, indicating alkanes. The absorption peak between 1780 and 1640cm^{-1}, represented the C=O stretching vibration, indicating the presence of ketones, aldehydes or esters. This indicates the presence of ketones, aldehydes and esters group in the oil.

Table 4 Compounds speciated in the catalytic pyrolysis oil produced in the integral test plant with *in situ* test rig

Compounds	Retention Time	Average Relative Concentration (%)
p-cymene	5.392	0.2
limonene	5.592	0.15
2-methylphenol	5.975	0.17
p-cresol	6.504	0.36
1-methyl-4-isopropenylbenzene	6.817	0.16
1,2,3,4-tetramethylbenzene	7.633	0.21
p-methylacetophenone	8.908	0.39
4,6-Dimethylindan	9.350	0.29
1,1-dimethyl-2-propenyl benzene	9.592	0.21
1,2-dihydro-3-methylnaphtalene		
2-Methylnapthalene	11.242	0.28
1,4-Dimethylazulene	12.067	0.55
1,3-Dimethylnaphtalene	15.175	1.16
2,3,5-Trimethylnapthalene	15.633	0.64
$C_{13}H_{14}$	18.533	1.18
$C_{13}H_{14}$	18.983	0.78
$C_{14}H_{16}$	19.308	0.53
$C_{14}H_{16}$	21.468	0.85
$C_{14}H_{16}$	22.325	0.61
$C_{14}H_{16}$	22.408	0.38
Isobutyl phthalate	23.008	0.63
$C_{12}H_{20}$	26.292	1.26
$C_{21}H_{34}O_2$	27.241	0.89
1,2-Benzenedicarboxylic acid, bis(2-	27.967	0.52
ethylhexyl) ester	39.367	2.84

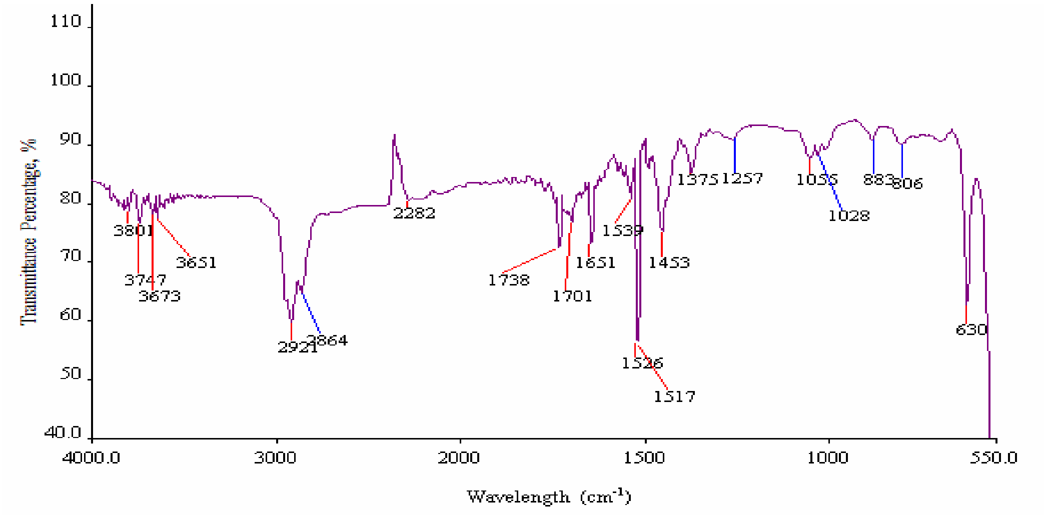

Figure 3 Spectra of pyrolysis oil derived from catalytic pyrolysis of rubber gloves at the integral test plant with *in situ* test rig

Likewise, the upgraded oil obtained in the *ex-situ* test rig, was also analyzed using GCMS and FTIR. Table 5 summarized the compounds presence in the upgraded oil produced using *ex situ* test rig. The analysis revealed that the dimer, trimer and tetramer compounds in the black pyrolysis oil diminished and vanished completely while new peaks emerged, corresponding to hydrocarbon compounds. However, the main constituent of the oil still remained as 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester of 11.13%. The chromatogram suggests that dimer, trimer and tetramer group of compounds that were initially in the black pyrolysis oil were cracked into straight chain hydrocarbons. These straight chain hydrocarbons were identified to be tetradecane (3.14%), hexadecane (4.94%), octadecane (6.74%), eicosane (7.89%), docosane (8.63%), tetracosane (8.29%), hexacosane (7.51%) and octacosane (6.44%). Therefore, the results of this study indicate that it is possible to deoxygenate pyro-oil product in order to obtain an enriched hydrocarbon of diesel-like fuel. This is in line with the observations made by Lima [15].

Table 5 Compounds speciated in the upgraded oil obtained in *ex situ* test rig

Compounds	Retention Time	Relative Concentration (%)
Dimethylnapthalene	15.250	0.79
2,4,6-Trimethylazulene ($C_{13}H_{14}$)	18.139	1.18
Isobutyl Phatalate	25.897	2.28
Tetradecane	31.858	3.14
Hexadecane	34.862	4.94
Octadecane	37.65	6.74
1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	39.018	11.13
Eicosane	40.244	7.89
Docosane	42.658	8.63
Tetracosane	44.931	8.29
Hexacosane	47.062	7.51
Octacosane	49.167	6.44

Figure 4 exemplified the FTIR spectra of the catalytically upgraded oil in the ex-situ test rig. The spectra of the upgraded oil showed several conspicuous, sharp and strong bands. The strong band at 1740cm^{-1} region, relate to the presence of ketones, aldehydes and ester group which is due the C=O stretching vibrations. The presence of esters groups is further confirmed by the presence of two or more bands in the region 1300-1000cm^{-1}, which represent the C-O stretch. The oil-spectra showed sharp and strong of absorption peak at 1235cm^{-1} and at 1044cm^{-1}, hence this confirms the presence of aliphatic esters in the pyrolysis oil which presence in large quantities. Both spectrums also show two strong bands between 1450cm^{-1} and 1370cm^{-1}, indicating C-H scissoring and bending which can be associated with the presence of alkanes group. This can be associated to the presence of eicosane, docosane, tetracosane, hexacosane and octacosane which were previously speciated by GCMS. Presence of aromatics is also noted based on the absorption band between 915cm^{-1} to 650cm^{-1}. The sharp and strong band at 1517cm^{-1} can be associated to the aromatic nucleus. However, these bands are small, indicating small concentration of aromatics in the upgraded oil.

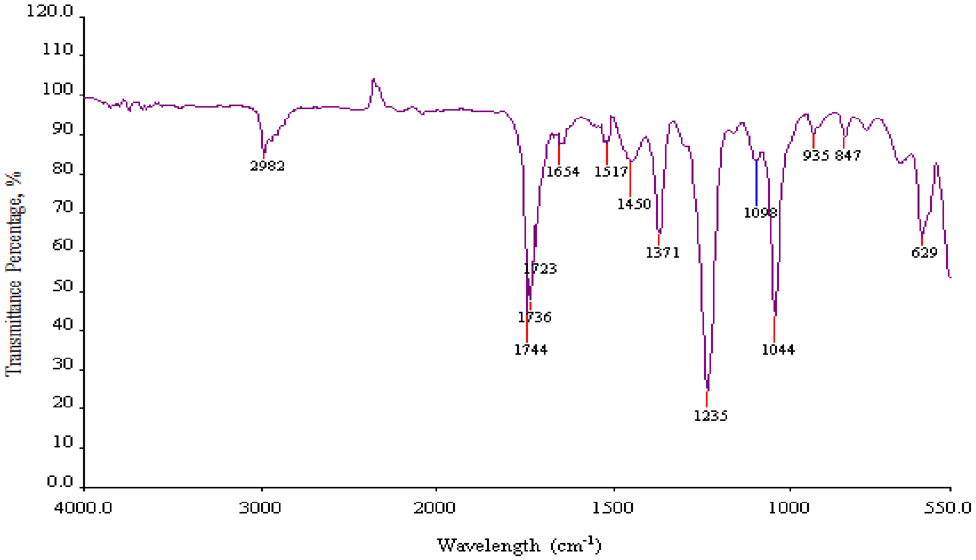

Figure 4 FTIR spectra of upgraded oil produced at 300°C using *ex-situ* test rig

4.0 CONCLUSION

Upgrading of pyrolysis oil into diesel-like fuel over zeolite was achieved in the *ex situ* test rig. This indicates that the pyrolysis oil was deoxygenated upon heating and passing through a catalyst column, resulting in straight chain hydrocarbons of diesel formulation like eicosane, docosane, tetracosane, hexacosane and octacosane. The aromatic compounds in the pyrolysis oil were also being cracked resulting in the absence of trimer, tetramer and pentamer group of aromatics in the upgraded oil. A change in the oil color was also observed, whereby the initial black pyro-oil color had changed into yellow hue. The overall yield of diesel-fuel like from pyrolyzing rubber gloves is 17.4wt%. Hence, it is concluded that upon upgrading, the black oil obtained from pyrolysis of the rubber glove is feasible to be converted into diesel-like fuel. However, the low overall yield called for further evaluation in order to assess the economic viability of the process.

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